III.A.20 Reliable Seals for Solid Oxide Fuel Cells

Objectives

- Develop reliable, cost-effective sealing techniques for solid oxide fuel cells (SOFCs).
- Determine performance-limiting features of sealing methods.
- Optimize seal properties.
- Determine seal degradation mechanisms and predict useful seal lifetimes.

Approach

- We are making glass matrix composite seals with a wide range of chemical and mechanical properties.
- The composite approach allows glass and filler properties to be optimized independently.
- Seal thermal and mechanical strains are reduced by selecting glass compositions with glass transition temperatures (Tg) below the SOFC operating temperature.
- Viscosity, coefficient of thermal expansion (CTE), and other seal characteristics can be tailored by adding unreactive powder.
- The volume fraction of the glass phase can be reduced to a minimum for the seal, which reduces reactivity with fuel cell materials.

Accomplishments

- We have made over 30 different glass compositions with potential for the composite seal approach and measured their physical properties.
- We have modified our glass compositions to provide better control over flow and thermal expansion properties.
- A new high temperature optical-mechanical measuring instrument (TOMMI) allowing in-situ video recording of specimens at elevated temperatures (to 1,700°C) has been purchased and set up and is being used to measure glass viscosities and to determine the effect of additive powder composition, size, and aspect ratio on composite seal flow and adhesion.
- A series of 2,000-hour tests at 750°C in air of two glass-ceramic compositions on two ferritic SS alloys (Ebrite and Crofer), on YSZ, and on anode material have been completed.
- One of our glass compositions (Glass 14A: 40% B_2O_3, 10% Al_2O_3, 10% BaO, 20% MgO, 20% CaO) was studied for reactivity with SS alloys (Crofer and 410 SS).

Ronald E. Loehman (Primary Contact), Bryan Gauntt, Alicia Ayala, Erica Corral, Raja Shah
Sandia National Laboratories, MS 1349
Albuquerque, NM 87185-1349
Phone: (505) 272-7601; Fax: (505) 272-7304
E-mail: loehman@sandia.gov

DOE Project Manager:
Ayyakkannu Manivannan
Phone: (304) 285-2078
E-mail: Ayyakkannu.Manivannan@netl.doe.gov

Future Directions

- Conduct additional 2,000-hour tests to demonstrate long-term stability of the glass ceramic seals.
- The 2,000-hour test protocol will be expanded to include effects of water vapor on seal performance at 750°C.
- Develop screening test for adhesion of different seal compositions and processes.
- Conduct thermal cycling tests of anode-interconnect seals to improve long-term stability.
- Refine reaction studies of sealants with SOFC components.
- Perform more fundamental mechanical tests on composite seal materials at operating temperatures; e.g., flexural strength and fracture toughness.

Introduction

Developing reliable methods for sealing solid oxide fuel cell stacks presents the most challenging set of performance criteria in the entire field of ceramic joining. For SOFC applications, the requirements on the sealing method include:

- Adhesion of the sealing material to fuel cell components from room temperature to as high as 1,000°C.
- Ability to provide a leak-tight seal at the SOFC operating temperature.
- Ability to maintain a seal while accommodating strains from SOFC components with different coefficients of thermal expansion (CTEs).
- Lack of adverse reaction between the sealing material(s) and the fuel cell components.
- Chemical and physical stability of the sealant at temperatures up to 1,000°C in oxidizing and reducing atmospheres.

- Thermal shock tolerance
- Electrically insulating for some SOFC designs

All of the above properties must be maintained for SOFC operating lifetimes of up to 40,000 hours. The list is written in approximate order of decreasing stringency. That is, no matter what the SOFC design, the seal must be adherent and leak-tight. On the other hand, some stack designs may require joining only similar materials and, thus, a matched CTE seal may be sufficient. Note also that the requirements may be contradictory. For example, being leak-tight and adherent at high temperatures suggests a refractory, stiff sealant, which may work against the requirement for thermal strain accommodation. Such situations are common, and seal developers know that seal design is specific to a particular component geometry and usually requires compromises among competing requirements.

Approach

Under DOE sponsorship, this project is developing an approach to sealing SOFCs that can be tailored to the specific requirements of the vertical teams in the DOE/SECA (Solid State Energy Conversion Alliance) program. The technique combines extensive capabilities in ceramic joining and composites that have been developed at Sandia over the past 20 years. In our judgment, relief of thermal expansion mismatch stresses will require SOFC seals to incorporate either a ductile metal or a high-viscosity glass that can relieve stresses through viscous creep. Other design and operational constraints on SOFCs, which as discussed above frequently are in opposition, severely restrict the options for seal materials. Based on our prior experience in ceramic joining and on results obtained so far on this project, we believe we have greatest design flexibility using ceramic-filled glasses and metal-filled glass composites. We have demonstrated that we can control properties such as glass transition temperature and thermal expansion coefficient by varying the compositions, amounts, and microstructures of the different phases. The choices are guided by thermochemical and composite microstructural models that allow us to target specific seal properties for a given design. Several seal systems are showing promise in functional tests.

Results

We have made over 30 different glass compositions with potential for the composite seal approach and measured their physical properties. Our glasses exhibit a range of glass transition temperatures (Tg), coefficients of thermal expansion (CTE) and viscosities, potentially applicable to a wide range of properties that may be appropriate for different SOFC component materials.

Our approach to SOFC sealing techniques consists of engineering ceramic-filled glass composites, metal-filled glass composites, and/or ceramic-filled metal composites that can meet SOFC requirements.

Glass composite seal materials were made using both zirconia (ZrO_2) and silver particles suspended in a glass composition previously found not to react with solid SOFC components including the YSZ electrolyte, the Ni-YSZ anode, and several potential stainless steel interconnect materials. The effects of the particle phases on the viscosity of the resulting composites were determined using a new high temperature optical-mechanical measuring facility (TOMMI) that allows in-situ video recording of specimens at elevated temperatures (up to 1,700°C). A parallel plate viscometer setup (Figure 1) was used to determine the

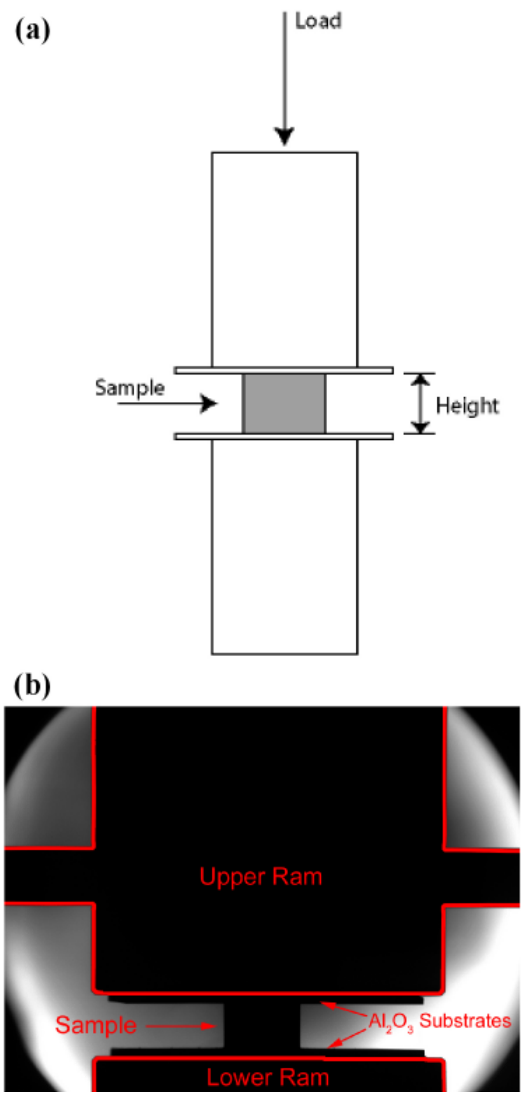

FIGURE 1. Parallel Plate Viscometer Setup Used for Viscosity Measurements; (a) Parallel Plate Viscometer; (b) Furnace Setup

effect of additive powder composition, size, and aspect ratio on composite seal flow and adhesion.

Composite viscosity was found to increase with an increased volume fraction of either metal or ceramic particles. The added particles increased the available surface area for wetting by the glass and helped retain the glass in the composite seal material. The effect of the YSZ filler was compared to that of Ni additions to the glass. We have shown that YSZ fillers have a greater effect on viscosity than added Ni because the YSZ nucleates glass crystallization (Figure 2).

The addition of ceramic particles also altered the glass crystallization behavior. The crystallization kinetics of the pure glass and the metal and ceramic composites were studied using differential thermal analysis. It was found that the ceramic particles had a much greater effect on the crystallization of the glass than the metal additives. The crystallization of the glass resulted in an increased volume fraction of refractory particles in the glass seal and a corresponding increase in the seal viscosity beginning at the onset of the crystallization.

The viscosity results were fit using classical suspension rheology models. The viscosity data, coupled with the suspension rheology models, gave us an increased understanding of the effects of added particles on the viscosity of the composite seal materials. A wide range of temperature-viscosity behaviors can be attained using the glass composite approach, and the constraints imposed by a pure glass seal approach can be overcome with the selective addition of a solid particle phase.

Having gained an understanding of how to engineer glass-ceramic viscosity, the reactivity and long-term stability of the composites was addressed. A series of 2,000-hour tests at 750°C in air of two glass-ceramic compositions (Glass 14a and Glass 14a +10% YSZ) on two ferritic SS alloys (Ebrite and Crofer) and on anode material have been completed. A detailed microprobe analysis of the samples was performed to determine the long-term stability of the composite seal and the substrates (Figure 3). Complex borate, Ca/Al, and Mg phases were identified in both glass compositions on the three different substrates. Ni diffusion was not observed along the interface in any case. The absence of appreciable reactions and Ni diffusion indicate long-term stability of the glasses at 750°C.

One of our glass compositions (Glass 14A: 40% B_2O_3, 10% Al_2O_3, 10% BaO, 20% MgO, 20% CaO) was studied for reactivity with SS alloys (Crofer and 410 SS). Testing conditions were (1) 850°C for 5 hours and (2) 850°C for 5 minutes and 750°C for 24 hours. Microprobe analysis shows the formation of a Cr_2O_3 layer along the glass/metal interface, the occurrence of complex boron phases in the bulk glass,

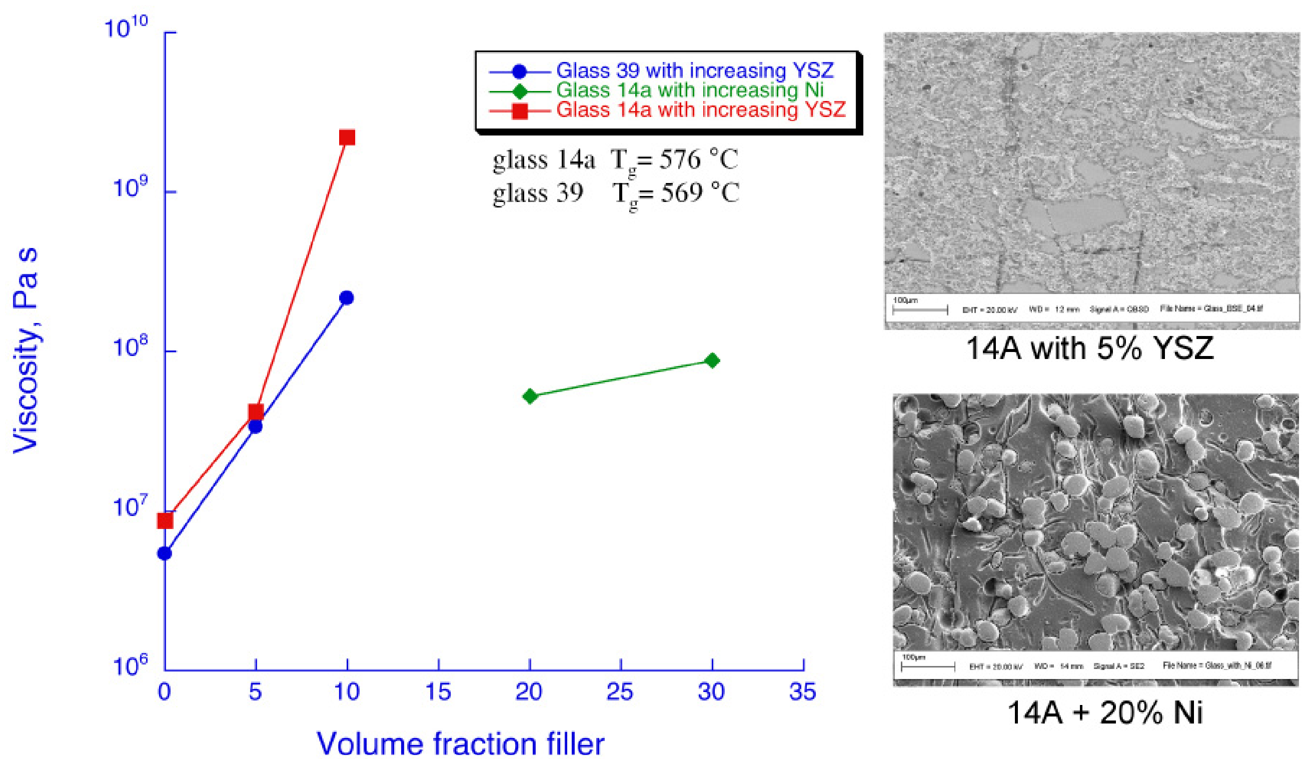

FIGURE 2. Glass-ceramic composite viscosity increases with increasing volume fraction of fillers. YSZ fillers have a greater effect on viscosity than added Ni because YSZ nucleates glass crystallization.

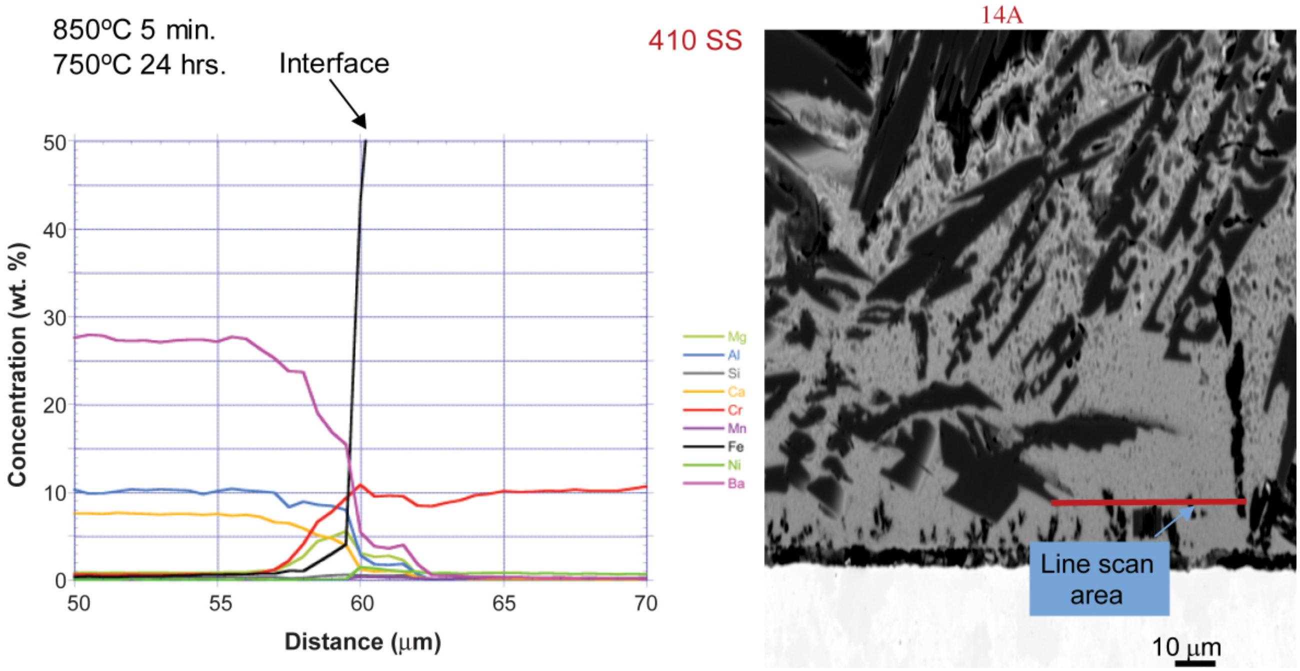

FIGURE 3. Electron microprobe analysis shows that glass 14A in contact with 410 SS forms Cr_2O_3 layer at interface and complex boron oxide phases in the bulk glass.

and Fe migration into the glass. This suggests that the glass-ceramic/SS combination is not stable for longer exposure time at higher temperatures.

Conclusions and Future Directions

Our work has demonstrated that glass composites are a favorable method for joining solid oxide fuel cell components. We have shown that seal properties can be varied to satisfy design criteria and materials constraints in SOFCs by varying the compositions, volume fractions, and microstructures of the different phases. Properties can be targeted using models that incorporate thermophysical data that are being obtained as part of the project. Long-term tests under representative SOFC operating conditions that are presently underway are providing compatibility data that will be used to decide whether seal compositions need to be tweaked to improve high temperature stability. Future work will be directed to detecting possible reactions, elucidating degradation mechanisms, and optimizing the seal system to ameliorate them. We also plan to test additional glasses and powder additives to qualify composite combinations with an even wider range of seal properties.

FY 2006 Publications/Presentations

1. R.E. Loehman, B. Gauntt, A. Ayala, and E. Corral, “Development of Glass-Ceramic Composites for Sealing Solid Oxide Fuel Cells”, Invited speaker, 30th Meeting of the American Ceramic Society (Cocoa Beach), January 25, 2006.

2. R.E. Loehman, A. Ayala, M. Brochu, and B. Gauntt, “Sealing Solid Oxide Fuel Cells with Glass-Matrix Composites,” 3rd International Brazing & Soldering Conference (IBSC) (ASM International), April 23-26, 2006, San Antonio, TX.